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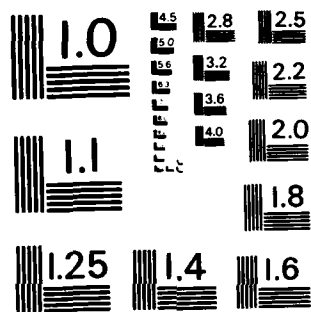
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TECHNICAL REPORT NO. 121

The Simultaneous Conversion of Ni-PR<sub>3</sub> and B-H to Ni-H and B-PR<sub>3</sub> Linkages  
by Thermal Rearrangement of d<sup>8</sup>-Closo-Bis(triarylphosphine)Nickelacarboranes.  
Crystal and Molecular Structure of [Closo-3-μ-CO-8-PPh<sub>3</sub>-3,1,2-NiC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sub>2</sub>;  
A Dimeric Nickelacarborane Complex Containing a Metal-Metal Bond.

By

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M. Frederick Hawthorne\*

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### Abstract

→ The reaction of  $L_2NiCl_2$  ( $L = PR_3$ ) species with *nido*-7,8-, -7,9-, or -2,9- $C_2B_9H_{11}^{2-}$  ions led to the formation of the corresponding icosahedral bis(phosphine)nickelacarboranes in high yield. Heating members of the *closo*-3,3-(triarylphosphine) $_2$ -3,1,2- $NiC_2B_9H_{11}$  series at 80° C in benzene solution led to the formation of the corresponding [*closo*-3,8-(triarylphosphine) $_2$ -3-H-3,1,2- $NiC_2B_9H_{11}$ ] by interchange of phosphine and hydrido ligands. No intermediates were observed and the reaction was specific for the bis(triarylphosphine)-3,1,2- $NiC_2$  icosahedral system among those investigated. A dimeric nickelacarborane carbonyl [*closo*-(-3- $\mu$ -CO-8- $PPh_3$ -3,1,2- $NiC_2B_9H_{11}$ ) $_2$ ] was prepared by a variety of routes such as the reaction of [*closo*-3,3-( $PPh_3$ ) $_2$ -3,1,2- $NiC_2B_9H_{11}$ ] (1a), with CO in benzene at 80° C. A variety of ligand substitution reactions were carried out with 1a. The mechanism of the phosphine-hydride ligand interchange is discussed. The dimeric nickelacarborane complex was characterized by an X-ray diffraction study. Amber crystals were triclinic, space group  $P\bar{1}$ , with  $a = 13.319(4)$ ,  $b = 10.039(3)$ ,  $c = 9.813(3)$  Å,  $\alpha = 80.00(1)^\circ$ ,  $\beta = 82.91(1)^\circ$ ,  $\gamma = 110.32(1)^\circ$ , and  $Z = 1$ . The structure was solved by conventional heavy atom methods to a final discrepancy index of  $R = 0.057$  for 2233 independent observed reflections. The complex contains a metal-metal bond (2.477(2) Å) and two metal-bridging carbon monoxide groups.

We have previously reported the formation of the closo-hydridonickelacarborane complex 1b through an unusually facile thermolysis of the closo-bis(triphenylphosphine)nickelacarborane complex 1a.<sup>1</sup> The reaction involved the interchange of a nickel-bound phosphine with the hydrogen atom of an adjacent boron vertex of the dicarbollide ligand thereby forming B-P and Ni-H bonds, respectively (Fig. 1). This type of ligand interchange reaction has also been demonstrated with phosphinerhoda-<sup>2</sup> and ruthenacarborane<sup>3</sup> complexes in these laboratories and with phosphineplatinacarborane<sup>4</sup> complexes elsewhere. In an attempt to establish the possible mechanism and scope of these reactions, a series of closo-bis(phosphine)nickelacarboranes were prepared and characterized (Fig. 2).

### Results and Discussion

Reaction of the respective nido-7,8-, -7,9-, or -2,9- $C_2B_9H_{11}^{2-}$  ions<sup>5</sup> with the appropriate bis(phosphine)nickeldihalide in dichloromethane ( $Tl_2$  salt) or tetrahydrofuran ( $Na_2$  salt) afforded the bis(phosphine)nickelacarborane complexes 1-6, 9 and 10 in high yield. Of the bis(phosphine)nickelacarborane complexes prepared, only the bis(tricyclohexylphosphine)nickelacarborane complex was unstable yielding  $HPCy_3^+ [closo-3,1,2-Ni(C_2B_9H_{11})_2]^-$ <sup>6</sup> (Cy = cyclohexyl,  $C_6H_{11}$ ) and nickel metal via a disproportionation reaction.

### Ligand Dissociation and Substitution Reactions with

Bis(triarylphosphine)nickelacarboranes. It was observed in  $^{31}\text{P}\{^1\text{H}\}$  nmr experiments performed at  $-23^\circ\text{C}$  that dichloromethane solutions of the bis(triarylphosphine)nickelacarboranes, **1a**, **2a**, **9** and **10**, exhibited not only their characteristic resonance(s), but also those of free triarylphosphine. With **1a** and **2a**, two additional resonances were observed downfield from the parent complex, as well, and at temperatures higher than  $30^\circ\text{C}$ , these downfield resonances broadened as the resonance due to free  $\text{PPh}_3$  disappeared into the baseline. Addition of a fractional molar equivalent of the respective triarylphosphine ligand resulted in the immediate disappearance of the two downfield resonances which presumably correspond to mono-phosphinenickelacarborane complexes. The remaining nickelacarborane complexes **3-8** did not exhibit a similar ligand dissociation process.

Ligand substitution reactions utilizing  $[\text{closo-3,3-(PPh}_3)_2\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}]$ , **1a**, resulted in the preparation of the monosubstituted complexes,  $[\text{closo-3-CO-3-PPh}_3\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}]$  ( $\nu\text{ CO} = 2050\text{ cm}^{-1}$ ), (**7**), and  $[\text{closo-3-C}_5\text{H}_5\text{N-3-PPh}_3\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}]$  ( $\nu\text{ C}_5\text{H}_5\text{N} = 1610\text{ cm}^{-1}$ ), (**8**) by reacting dichloromethane solutions of **1a** with carbon monoxide or pyridine, respectively. Mixed triarylphosphine complexes could be generated in situ by the addition of 2.2 molar equivalents of  $\text{P(p-tol)}_3$  to dichloromethane solutions of **1a**. The resonances observed suggested the presence of  $[(\text{P(p-tol)}_3)(\text{PPh}_3)\text{NiC}_2\text{B}_9\text{H}_{11}]$ ,  $[(\text{PPh}_3)_2\text{NiC}_2\text{B}_9\text{H}_{11}]$ , and  $[(\text{P(p-tol)}_3)_2\text{NiC}_2\text{B}_9\text{H}_{11}]$  in an equilibrium mixture of approximately 1:1:1 (along with free  $\text{PPh}_3$  and  $\text{P(p-tol)}_3$ ). The equilibria could be shifted in either direction by the addition of an excess of the respective phosphine ligand. Attempts to isolate the mixed

tertiary phosphine complex by either column chromatography or fractional crystallizations were unsuccessful. Strongly basic ligands such as triethylphosphine quantitatively displaced the triphenylphosphine ligands from the nickel vertex of **1a**.

Thermal Rearrangement of Bis(triarylphosphine) Nickelacarboranes.

The complexes **1-10** were heated in benzene at the reflux temperature for up to 3 d to determine their ability to undergo the ligand interchange reaction (Fig 1). The surprising result was that only those icosahedral nickelacarboranes which had the 3,1,2-NiC<sub>2</sub> configuration and two triarylphosphine ligands at the formal Ni(+2) vertex were subject to the ligand interchange reaction under the conditions employed here.

In another set of experiments the progress of the phosphine-hydride migration reaction was monitored by <sup>31</sup>P{<sup>1</sup>H} FTNMR at 80°C in benzene solutions of **1a**. The resonances assigned to the product were observed to grow in smoothly at the expense of the resonance assigned to the starting material. Other resonances which might be associated with the buildup of an intermediate species were not observed. The final spectrum showed two distinctly different resonances that could be easily distinguished as Ni-P (sharp singlet) and B-P (broad quartet) linkages, respectively. The solubility of **1a** in aromatic solvents was limited and precluded the possibility of performing meaningful kinetic experiments.

Reactivity of the Nickel-Hydride Complex, **1b**. The nickel-hydrogen bond in complex **1b** reacted, as expected, with chlorinating agents.<sup>7</sup> Dichloromethane solutions of **1b** reacted immediately with dry hydrogen chloride to give [closo-3,8-(PPh<sub>3</sub>)<sub>2</sub>-3-Cl-3,1,2-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], **11**.



Thermolysis of **1b** in chlorinated solvents such as dichloromethane or chloroform also gave **11**. The  $^{11}\text{B}(^1\text{H})$  nmr of **11** clearly showed the B-P coupling (127 Hz); unfortunately, the positional assignment of the phosphorus-substituted boron atom could not be obtained from this spectrum and the structure of **11** was proven by syntheses described below.

Degradation of the nickel-hydride complex, **1b**, in hot glacial acetic acid gave  $\text{PPh}_3$ ,  $\text{Ni}(\text{OAc})_2$ , and the phosphine substituted carborane [**nido**- $\text{PPh}_3\text{-C}_2\text{B}_9\text{H}_{11}$ ], **12**, in high yield. The B-P coupling ( $J = 125$  Hz) was observed in the  $^{11}\text{B}\{^1\text{H}\}$  nmr spectrum and the ratio of the resonances suggested that the formation of the B-P bond had occurred on a plane of molecular symmetry. Similar ligand substituted carboranes have been obtained by the oxidative substitution of nitrogen, oxygen, and phosphorus donor ligands to [**nido**-7,8- $\text{C}_2\text{B}_9\text{H}_{12}$ ] $^-$  carborane ions in the presence of  $\text{FeCl}_3$ .<sup>8</sup> It should be noted that the overall transformation of [**nido**-7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ] $^{2-}$  ion to **12** occurs in high yield and is regiospecific, in contrast to the oxidative substitution reaction with  $\text{FeCl}_3$  which produces mixtures of ligand-substituted carborane isomers. The neutral ligand-substituted carborane reacted quickly with strong bases such as sodium hydride to liberate hydrogen and form the [**nido**-10- $\text{PPh}_3\text{-7,8-C}_2\text{B}_9\text{H}_{10}$ ] $^-$  ion. The latter ion reacted with  $(\text{PPh}_3)_2\text{NiCl}_2$ , affording **11** in high yield, (Fig. 3).

Complex **1b** reacted with carbon monoxide at  $80^\circ\text{C}$  to produce  $\text{H}_2$  and a compound formulated as  $[\text{Ni}(\text{CO})(\text{PPh}_3)\text{C}_2\text{B}_9\text{H}_{10}]_2$ , **13**, [ $\nu\text{ CO} = 1850\text{ cm}^{-1}$ ]. Alternatively, **13** could also be prepared by heating benzene solutions of **1a**, or **7**, in the presence of carbon monoxide, (Fig 4).

Since the B-P coupling (120 Hz) observed in the  $^{11}\text{B}\{^1\text{H}\}$  nmr spectrum was uninformative with respect to the assignment of the site of  $\text{PPh}_3$  substitution, an X-ray crystallographic investigation of the dimeric nickelacarborane complex, **13**, was performed.

The molecular structure of  $[\text{clos-3-}\mu\text{-CO-8-PPh}_3\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{10}]_2$ , **13**, is shown in Figure 5 from which the boron atom attached to the triphenylphosphine ligand is identified as the unique boron atom, B(08), in the bonding face of the carborane cage. The metal-metal bond in **13** is most reasonably interpreted as a single bond based on its distance and the effective atomic number of eighteen for the metal center. The nickel-nickel bond is also supported by two bridging carbon monoxide molecules related by a crystallographic center of symmetry. The formal nickel (I) vertex is a  $d^9$  metal center, and therefore asymmetric nickel-carborane bonding was expected as observed with other electron-rich metallocarborane complexes.<sup>9</sup> However, the Ni atom is symmetrically bound to the bonding face of the carborane ligand. Based on calculations by Mingos and Hoffman,<sup>10</sup> icosahedral metallocarborane complexes containing metal centers that are considered to be electron rich should have distorted polyhedra. In addition, a variety of crystallographic investigations on metallocarboranes with electron-rich metal vertices clearly show deformations of the carborane cage.<sup>11</sup> This seeming contradiction can be most easily rationalized by recognizing that the carbon monoxide molecules bonded to the two nickel atoms are available as excess electron density sinks via back-bonding. This has been observed with another electron-rich metallocarborane complex which contained carbon monoxide as a ligand.<sup>12</sup>

In a structural sense, the nickelacarborane dimer (13) is more closely related to the isoelectronic species,  $[\eta-(C_5H_4CH_3)-\mu-(CO)Ni]_2$  than to the unsubstituted analog,  $[\eta-(C_5H_5)-\mu-(CO)Ni]_2$ .<sup>13</sup> The  $CH_3$ -cp dimer and 13 each have a coplanar arrangement of the Ni atoms and the carbonyl groups. This planarity is missing in the unsubstituted cp dimer where the carbonyl oxygen atoms deviate greatly from the plane.<sup>13</sup> In 13, the oxygen atom of each bridging carbonyl group is only 0.040(7) Å from the Ni-C-Ni-C plane. The  $[(CH_3cp)NiCO]$  dimer was observed to have a Ni-Ni bonding distance of 2.390(1) Å, in comparison to 2.477(1) Å in the nickelacarborane dimer. This structure determination also confirms the position of  $PPh_3$  substitution seen in 11 and 12, above.

Mechanism of the Ligand Interchange Reaction. In the absence of kinetic data any discussion of the mechanism of the phosphine-hydride interchange reaction lacks precision. However, the fact that this reaction is only observed with icosahedral nickelacarboranes of the 3,1,2- $NiC_2$  configuration and only with triarylphosphine ligands attached to the metal vertex suggests that phosphine dissociation is an important initial equilibrium which is followed by attack of the free phosphine upon the BH vertex (8). This scheme is presented in Fig 6. The reason for the peculiar susceptibility of this particular boron atom in the 3,1,2- isomer is presently obscure. Although the ligand interchange reaction is shown as a concerted process in Fig 6, it is possible that a  $Ph_3PB-H-BH$  bridge array could be present in the open face of a nido-intermediate produced by nucleophilic attack of free  $PPh_3$  at vertex 8 of the [hypercloso-3-( $PPh_3$ )-3,1,2- $NiC_2B_9H_{11}$ ]<sup>14,15</sup> formed by the initial phosphine dissociation. Formation of this nido-intermediate could be

accompanied by elimination of formal Ni(0) which, in turn, could oxidatively add to the B-H-B bridge bond of the nido-species. These schemes may also be applicable to the mechanisms of the ligand interchange reactions observed with other metals.<sup>2,3,4</sup> Further work of a mechanistic sort is clearly warranted.

## Experimental Section

**Methods and Materials.** The infrared spectra were measured as Nujol mulls on sodium chloride plates using a Perkin-Elmer 137 spectrophotometer. The  $^1\text{H}$  (200.133 MHz) and  $^{31}\text{P}\{^1\text{H}\}$  (81.02 MHz) nuclear magnetic resonance spectra were recorded on a Bruker WP200 Fourier transform instrument. The signal at 5.28  $\delta$ , corresponding to  $\text{CH}_2\text{Cl}_2$  (Merck), was used as an internal reference for proton NMR spectra. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were referenced externally to  $\text{H}_3\text{PO}_4$ , shifts were then corrected for the deuterated solvent used and the chemical shift of  $\text{PPh}_3$  was taken as  $-6.0$  ppm. The  $^{11}\text{B}$  and  $^{11}\text{B}\{^1\text{H}\}$  (126.7 MHz) nmr spectra were measured on an instrument designed and built by F.A.L. Anet of this department utilizing  $\text{BF}_3\cdot\text{OEt}_2$  as an external standard. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories (Woodside, New York).

Reactions were carried out under an argon (Liquid Carbonic) atmosphere using standard techniques for handling air sensitive materials and all solvents (Mallinkrodt) were dried, deoxygenated, and distilled from appropriate drying agents<sup>16</sup> before use.

Literature methods were used to prepare  $[\text{closo-7,8-(TiCl}_2\text{B}_9\text{H}_{11})\text{Ti}]$ ,<sup>17</sup>  $(\text{CH}_3)_3\text{NH}^+[\text{nido-7,9-C}_2\text{B}_9\text{H}_{12}]^-$ , and  $(\text{CH}_3)_3\text{NH}^+[\text{nido-2,9-C}_2\text{B}_9\text{H}_{12}]^-$ .<sup>5</sup>  $(\text{PPh}_3)_2\text{NiCl}_2$  and  $(\text{P}(p\text{-tol})_3)_2\text{NiCl}_2$  were prepared by boiling  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  and a four fold excess of the respective phosphine ligand in *n*-butanol for four hours. The black crystalline product was separated from the mother liquor by filtration while the solution was warm, washed generously with ethanol, heptane, and diethyl

ether, and dried under vacuum overnight.  $(\text{PEt}_3)_2\text{NiCl}_2$ ,  $(\text{PPh}_2\text{Me})_2\text{NiCl}_2$  and  $(\text{PPhMe}_2)_2\text{NiCl}_2$ , and  $(\text{DPPP})\text{NiCl}_2$  ( $\text{DPPP} = \text{PPh}_2(\text{CH}_2)_3\text{PPh}_2$ ) were prepared by reacting a warm ethanolic solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with the appropriate phosphine ligand under an inert atmosphere. The red-colored crystalline products were separated by Schlenk filtration, washed liberally with heptane and diethyl ether, and dried under vacuum overnight.

Reagents such as  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , glacial acetic acid (Mallinkrodt),  $\text{PPh}_3$ ,  $\text{PEt}_3$ ,  $\text{PPh}_2\text{Me}$ ,  $\text{PPhMe}_2$ ,  $\text{P}(p\text{-tol})_3$  (Aldrich),  $\text{PCy}_3$ , bis-1,3-diphenylphosphinopropane (Strem), and  $\text{NaH}$  (Alfa) were all commercially available and used without further purification.

Carbon monoxide (Liquid Carbonic) and hydrogen chloride (Matheson) were purified by passing the reagent gases through  $\text{H}_2\text{SO}_4$  and then over  $\text{KOH}/\text{CaSO}_4$ . Pyridine (Aldrich) was distilled from  $\text{KOH}$ .

General Procedure for the Preparation of  
 $[\text{Closso-3,3-(Phosphine)}_2\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}]$  Complexes. Stirring the appropriate bis(phosphine)nickel dichloride complex (2.00 mmol) and thallous dicarbollide (1.08 gm, 2.00 mmol) in dichloromethane (200 ml) gave dark green solutions while the white  $\text{TlCl}$  precipitated from the reaction mixture. Schlenk filtration and dilution with heptane afforded crystalline product. Reactions were usually complete within two hours. Two recrystallizations from dichloromethane/heptane gave analytically pure complexes as large, non-solvated, crystalline blocks.

$[\text{Closso-3,3-(PPh}_3)_2\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}]$ , 1a. Using  $(\text{PPh}_3)_2\text{NiCl}_2$  (1.31

gm, 2.00 mmol) and the procedure described above, the product was isolated as olive-green plates (1.13 gm, 1.58 mmol, 79%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.2-7.5 (envelope);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -19.44, -12.68, -9.11 (2:2:5);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 30.6 (s). Anal. Calcd. for  $\text{C}_{38}\text{H}_{41}\text{B}_9\text{P}_2\text{Ni}$ : C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.64; H, 6.28; B, 12.79; P, 7.95; Ni, 8.92.

$[\text{Closso-3,3-(P(p-tol))}_2]_2\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}$  1, 2a. Using  $(\text{P(p-tol)})_3\text{NiCl}_2$  (1.48 gm, 2.00 mmol) and the procedure described above, the product was isolated as an olive-green crystalline solid (1.28 gm, 1.60 mmol, 80%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  6.9-7.4 (envelope, 24 H), 2.29 (s, 18 H);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -19.84, -7.91 (2:7);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 28.7 (s). Anal. Calcd. for  $\text{C}_{44}\text{H}_{53}\text{B}_9\text{P}_2\text{Ni}$ : C, 66.06; H, 6.68; B, 12.17; P, 7.74; Ni, 7.34. Found: C, 66.30; H, 6.75; B, 12.33; P, 7.60; Ni, 7.59.

$[\text{Closso-3,3-(PEt)}_2]_2\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}$  1, 3. Using  $(\text{PEt})_3\text{NiCl}_2$  (0.73 gm, 2.00 mmol) and the procedure described above, the product was isolated as bright-green crystals (0.80 gm, 1.86 mmol, 93%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.68 (m, 12 H), 1.18 (m, 18 H), 1.88 (br s, 2 H);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -19.84, -13.08, -9.11, -4.73 (2:2:4:1);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 2.8 (s). Anal. Calcd. for  $\text{C}_{14}\text{H}_{41}\text{B}_9\text{P}_2\text{Ni}$ : C, 39.34; H, 9.67; B, 22.76; P, 14.49; Ni, 13.74. Found: C, 39.03; H, 9.75; B, 22.48; P, 14.78; Ni, 13.52.

$[\text{Closso-3,3-(PPh}_2\text{Me)}_2]_2\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{11}$  1, 4. Using  $(\text{PPh}_2\text{Me})_2\text{NiCl}_2$

(1.06 gm, 2.00 mmol) and the procedure described above, the product was isolated as dark-green crystals (1.06 gm, 1.80 mmol, 90%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.22-7.5 (envelope, 20 H), 1.70 (t, 6 H,  $J = 4.4$  Hz);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -19.04, -12.29, -8.71, -6.32, -2.75 (2:2:3:1:1);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 14.6 (s). Anal. Calcd. for  $\text{C}_{28}\text{H}_{37}\text{B}_9\text{P}_2\text{Ni}$ : C, 56.84; H, 6.30; B, 16.46; P, 10.47; Ni, 9.92. Found: C, 56.56; H, 6.38; B, 16.10; P, 10.53; Ni, 10.10.

[Clos0-3,3-(PPhMe<sub>2</sub>)<sub>2</sub>-3,1,2-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] 5. Using (PPhMe<sub>2</sub>)<sub>2</sub>NiCl<sub>2</sub> (0.81 gm, 2.00 mmol) and the procedure described above, the product was isolated as dark-green crystals (0.86 gm, 1.84 mmol, 92%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.43-7.63 (envelope, 10 H), 1.76 (br s, 2 H), 1.43 (t, 12 H,  $J = 4.9$  Hz);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -18.65, -11.89, -7.91, -2.75 (2:2:4:1);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 17.1 (s). Anal. Calcd. for  $\text{C}_{18}\text{H}_{33}\text{B}_9\text{P}_2\text{Ni}$ : C, 46.26; H, 7.12; B, 20.82; P, 13.25; Ni, 12.56. Found: C, 46.21; H, 7.07; B, 21.27; P, 12.92; Ni, 13.47.

[Clos0-3,3-(DPPP)-3,1,2-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] 6. Using (DPPP)NiCl<sub>2</sub> (1.08 gm, 2.00 mmol) and the procedure described above, the product was isolated as light-green plates (1.01 gm, 1.68 mmol, 84%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.32-7.7 (envelope, 20 H), 0.84-2.55 (envelope, 6 H), 1.74 (br s, 2 H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 14.8 (s). (The complex is almost insoluble in most solvents, and only slightly soluble in dichloromethane.) Anal. Calcd. for  $\text{C}_{29}\text{H}_{37}\text{B}_9\text{P}_2\text{Ni}$ : C, 57.70; H, 6.18; B, 16.12; P, 10.26; Ni, 9.73. Found: C, 57.59; H, 6.28; B, 16.53; P, 10.33; Ni, 10.07.



[Clos0-2,2-(PPh<sub>3</sub>)<sub>2</sub>-2,1,7-(or-2,1,12)-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] 1. The addition of 2.5 equivalents of NaH (0.12 gm, 5.00 mmol) to a tetrahydrofuran solution (250 ml) of the appropriate (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> [nido-7,9-(or 2,9)-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> carborane salts (0.39 gm, 2.00 mmol) resulted in the evolution of hydrogen gas. The solution was stirred while refluxing for 6 hrs and filtered under argon onto the (PPh<sub>3</sub>)<sub>2</sub>NiCl<sub>2</sub> complex (1.31 gm, 2.00 mmol). The reaction mixture was then stirred overnight at room temperature. Schlenk filtration was used to remove NaCl and dilution with heptane afforded the crystalline product. Three recrystallizations from dichloromethane/heptane gave analytically pure product.

[Clos0-2,2-(PPh<sub>3</sub>)<sub>2</sub>-2,1,7-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] 9. Using (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> [nido-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> and the procedure described above, the product was isolated as red-orange crystals (0.93 gm, 1.30 mmol, 65%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.03-7.72 (envelope, 30 H), 2.68 (br s, 2 H); <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) ppm -19.84, -15.74, -10.70, -2.75 (3:1:4:1); <sup>31</sup>P{<sup>1</sup>H} NMR (20% CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>) ppm 40.6 (d, J = 29 Hz), 25.7 (d). Anal. Calcd. for C<sub>38</sub>H<sub>41</sub>B<sub>9</sub>P<sub>2</sub>Ni: C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.18; H, 5.71; B, 14.30; P, 8.82; Ni, 8.34.

[Clos0-2,2-(PPh<sub>3</sub>)<sub>2</sub>-2,1,12-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] 10. Using (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> [nido-2,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> and the procedure described above the product was isolated as dull-green crystals (0.86 gm, 1.20 mmol, 60%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.11-7.47 (envelope, 30 H), 2.34 (br s, 1 H), 2.27 (br s, 1 H); <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) ppm -20.01, -14.85, -10.11, -8.12 (4:2:2:1); <sup>31</sup>P{<sup>1</sup>H} NMR (20% CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>) ppm 32.8 (s). Anal. Calcd. for

$C_{38}H_{41}B_9P_2Ni$ : C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.53; H, 6.05; B, 13.59; P, 8.78; Ni, 8.64.

General Procedure for the Preparation of

$[closo-3,8-(P(aryl)_3)_2-3-H-3,1,2-NiC_2B_9H_{11}]$  Complexes. A 300 ml Schlenk flask was charged with  $[closo-3,3-(P(aryl)_3)_2-3,1,2-NiC_2B_9H_{11}]$  (2.0 mmol) and a magnetic stirring bar. It was then fitted with a reflux condenser, vacuum evacuated, and then refilled with argon. Freshly distilled benzene (200 ml) was added via syringe. The migration reaction began when the solution was brought to the reflux temperature. The progress of the reaction was monitored by thin layer chromatography using Kodak fluorescent thin layer silica gel plates and benzene. The red product has a higher  $r_f$  value than the green starting material. Addition of heptane via syringe and volume reduction of the solution by vacuum evaporation afforded a red microcrystalline material. Further addition of heptane and volume reduction precipitated the product quantitatively. Three recrystallizations from dichloromethane/heptane gave the analytically pure product.

$[Closo-3,8-(PPh_3)_2-3-H-3,1,2-NiC_2B_9H_{11}]$ , 1b. Thermolysis of 1a (1.43 gm, 2.00 mmol), as described above, gave a red-orange crystalline product (0.84 gm, 1.18 mmol, 59%);  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  7.30-7.84 (envelope, 30 H), -8.40 (dd,  $J_1 = 91.6$  Hz,  $J_2 = 7.3$  Hz);  $^{11}B\{^1H\}$  NMR ( $CD_2Cl_2$ ) ppm -23, -15 (7:2);  $^{31}P\{^1H\}$  NMR (20%  $CD_2Cl_2/CH_2Cl_2$ ) ppm 24.4 (s), 2.7 (br q). Anal. Calcd. for  $C_{38}H_{41}B_9P_2Ni$ : C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.61; H, 5.84; B, 13.92; P, 8.60;

Ni, 8.13.

[Clos0-3,8-(P(p-tolyl))<sub>3</sub>]<sub>2</sub>-3-H-3,1,2-NiC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] 2b. Thermolysis of 2a (1.60 gm, 2.00 mmol), gave an orange-red crystalline product (0.96 gm, 1.22 mmol, 61%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.05-7.55 (envelope, 24 H), 2.33 (s, 9 H), 2.31 (s, 9 H), -8.59 (dd, 1 H, J<sub>1</sub> = 91.6 Hz, J<sub>2</sub> = 7.32 Hz); <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) ppm -23, -15 (7:2); <sup>31</sup>P{<sup>1</sup>H} NMR (20% CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>) ppm 22.4 (s), 2.0 (br q). Anal. Calcd. for C<sub>44</sub>H<sub>53</sub>B<sub>9</sub>P<sub>2</sub>Ni: C, 66.06; H, 6.68; B, 12.17; P, 7.74; Ni, 7.34. Found: C, 65.38; H, 6.71; B, 12.25; P, 7.29; Ni, 7.31.

**General Procedure for Ligand Exchange Reactions Using 1a.** A 250 ml Schlenk flask was charged with 1a (1.43 gm, 2.00 mmol) and a magnetic stirring bar. The flask was fitted with a rubber septum, vacuum evacuated, and refilled with argon. Dichloromethane (200 ml) was introduced via syringe.

[Clos0-3-CO-3-PPh<sub>3</sub>]-3,1,2-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] 7. Carbon monoxide was introduced into the solution via a syringe needle through the side arm and vented through a needle in the septum cap. The bubbling of carbon monoxide was continued until the reaction was complete (monitored by thin layer chromatography). Dilution with heptane and solvent removal by vacuum evaporation gave a lavender powder. Two recrystallizations from dichloromethane/heptane afforded the analytically pure red-violet crystalline product (0.84 gm, 1.74 mmol, 87%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.31-7.70 (envelope, 15 H), 2.05 (br s, 2 H); <sup>11</sup>B{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>) ppm

-22.62, -13.48, -10.30, -6.32 (3:2:2:2);  $^{31}\text{P}\{^1\text{H}\}$  (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 27.9 (s). Anal. Calcd. for  $\text{C}_{21}\text{H}_{26}\text{B}_9\text{PNiO}$ : C, 52.40; H, 5.44; B, 20.21; P, 6.43; Ni, 12.20. Found: C, 52.49; H, 5.37; B, 19.42; P, 6.28; Ni, 12.07.

[Closa-3- $\text{C}_5\text{H}_5\text{N}$ -3- $\text{PPh}_3$ -3,1,2- $\text{NiC}_2\text{B}_9\text{H}_{11}$ ], 8. Pyridine (10.0 gm, 126 mmol) was introduced via syringe and the solution was stirred overnight. The product precipitates as a green powder upon addition of heptane and volume reduction by rotary evaporation. Two recrystallizations from dichloromethane/heptane gave the analytically pure forest-green crystalline product (0.85 gm, 1.60 mmol, 80%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.56 (d, 2 H,  $J = 4.9$  Hz), 7.33-7.78 (envelope, 15 H), 6.9 (t, 3 H,  $J = 7.3$  Hz);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -20.24, -13.08, -9.50 (3:2:4);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 36.7 (s). Anal. Calcd. for  $\text{C}_{25}\text{H}_{21}\text{B}_9\text{PNiN}$ : C, 56.38; H, 5.87; B, 18.27; P, 5.82; Ni, 11.03; N, 2.63. Found: C, 56.41; H, 5.92; B, 18.56; P, 5.39; Ni, 10.88; N, 2.90.

#### General Procedure for the Preparation of

[Closa-3,8-( $\text{PPh}_3$ ) $_2$ -3-H-3,1,2- $\text{NiC}_2\text{B}_9\text{H}_{10}$ ], 1b Derivatives. A 250 ml Schlenk flask was charged with complex 1b (1.43 gm, 2.00 mmol) and a magnetic stirring bar and fitted with a reflux condenser. The system was vacuum evacuated and refilled with argon. Freshly distilled benzene (150 ml) was added via syringe.

[Closa-3-Cl-3,8- $\text{PPh}_3$ -3,1,2- $\text{NiC}_2\text{B}_9\text{H}_{10}$ ], 11. Hydrogen chloride was introduced into the solution via syringe needle through the side arm of the flask. A rapid red to violet color change indicated an immediate

reaction. Addition of heptane and removal of solvent by vacuum evaporation gave a purple powder. One recrystallization from dichloromethane/heptane give dark-purple crystalline product (1.22 gm, 1.62 mmol, 81%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.24-7.79 (envelope, 30 H), 3.38 (br s, 2 H);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -19.84, -10.70, -1.95 (d,  $J = 128$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 18.3 (s), 7.0 (br q). Anal. Calcd. for  $\text{C}_{38}\text{H}_{40}\text{B}_9\text{P}_2\text{NiCl}$ : C, 60.85; H, 5.38; B, 12.97; P, 8.26; Ni, 7.83; Cl, 4.73. Found: C, 62.03; H, 5.45; B, 13.03; P, 7.90; Ni, 7.96; Cl, 5.04.

[Nido-8-PPH<sub>3</sub>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] 12. Glacial acetic acid (50 ml) was added via syringe and the solution was brought to the reflux temperature. The reaction was complete after the red color of the starting material disappeared. Vacuum evaporation of the solution to dryness gave a tan microcrystalline precipitate. Two recrystallizations from dichloromethane/heptane gave a white crystalline product (0.54 gm, 1.38 mmol, 69%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  6.94-7.62 (envelope, 15 H), 2.56 (br s, 2 H);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -37.33, -33.35 (d,  $J = 136$  Hz), -20.24, -15.47, -11.09 (1:1:2:3:2);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 3.5 (br q). Anal. Calcd. for  $\text{C}_{20}\text{H}_{26}\text{B}_9\text{P}$ : C, 60.85; H, 6.64; B, 24.67; P, 7.85. Found: C, 60.60; H, 6.92; B, 24.90; P, 7.93.

[Closa-(-3-u-CO-8-PPH<sub>3</sub>-3,1,2-NiC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)] 13. Carbon monoxide was introduced via syringe needle through the side arm of the flask and the solution was brought to a gentle reflux. The reaction was monitored by thin layer chromatography and was complete in six to eight hours. The reaction mixture was rotary vacuum evaporated to dryness and the

precipitate was washed with heptane and dried under vacuum to give a red-copper powder (1.41 gm, 1.46 mmol, 73%). Two recrystallizations from dichloromethane/heptane gave analytically pure copper-colored crystalline product. The same procedure using complex **7** (0.96 gm, 2.00 mmol) afforded complex **13** (0.64 gm, 1.34 mmol, 67%);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.32-8.02 (envelope, 15 H), 2.64 (br s, 2 H);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) ppm -19.06, -15.30, -10.66, -7.03 (d,  $J = 132$  Hz) (2:4:2:1);  $^{31}\text{P}\{^1\text{H}\}$  NMR (20%  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ ) ppm 7.7 (br q). Anal. Calcd. for  $\text{C}_{21}\text{H}_{25}\text{B}_9\text{PNiO}$ : C, 52.40; H, 5.44; B, 20.21; P, 6.43; Ni, 12.20. Found: C, 51.99; H, 5.30; B, 19.55; P, 6.54; Ni, 12.26.

Collection and Reduction of X-ray Data. A transparent amber-copper crystal of **13** having approximate dimensions 0.30 x 0.15 x 0.06 mm was used for data collection. Preliminary photographs indicated no symmetry and no systematic absences, indicative of space group P1 or  $\bar{P}1$ . After mounting on an xyz goniometer, the crystal was optically centered on a Picker FACS 1 diffractometer equipped with a molybdenum tube ( $\lambda_{\text{K}(\alpha)} = 0.71069 \text{ \AA}$ ) and a zirconium filter. Preliminary unit cell parameters were determined from a least-squares refinement of the angular settings of 12 accurately centered reflections. The unit cell parameters are given in Table 1 as part of a summary of data for this study. The density, measured by flotation using distilled water/KI at 21°C, was  $1.265 \text{ gm/cm}^3$ , in reasonable agreement with the calculated density of  $1.29 \text{ gm/cm}^3$  for  $Z = 1$ . The 4271 reflections, including standards, were measured at 25°C over a two theta range of 0-50 degrees, using the theta-two theta scan method. Reflections were scanned at a

rate of 2 degrees/min over a range of  $2.2(1 + 0.692 \tan \theta)$ . Background was measured for 20 sec at each end of the scan. Of the reflections measured, 4133 were unique and of these 2233 were considered observed,  $I > 3 \sigma(I)$ . Two standard reflections were measured after every 100 reflections to monitor tube stability and possible crystal deterioration. There was no observable decay. Intensities were corrected as described previously<sup>18</sup> for Lorentz and polarization effects. An absorption correction was applied with an absorption coefficient ( $\mu$ ) of  $8.39 \text{ cm}^{-1}$  for Mo (K alpha) radiation.

Scattering factors for neutral nickel, phosphorus, carbon, and boron were taken from International Tables;<sup>19</sup> hydrogen scattering factors were obtained from Stewart, Davidson, and Simpson,<sup>20</sup> and the real and imaginary terms for anomalous scattering of Ni and P were taken from Cromer.<sup>21</sup> The function  $\sum_w ||F_{\text{obs}}| - |F_{\text{calc}}||^2$  was minimized in least squares refinement.

Solution and Refinement of the Structure. The x, y, and z coordinates for the crystallographically unique Ni and P atoms were deduced from the Patterson map. The heavy atom method allowed successive location of all of the non-hydrogen atoms by iterative least squares and Fourier calculations (all cage atoms were given boron scattering factors). The positions of the polyhedral carbon atoms were easily recognized by their shorter bond lengths and their smaller temperature factors and were assigned carbon scattering factors. Further least-squares refinement reduced R to 0.068 and  $R_w$  to 0.070, and a difference Fourier synthesis indicated the positions of all the hydrogen atoms. Least-squares refinement of the positional parameters of all the

atoms and the anisotropic thermal parameters of the heavy atoms and isotropic parameters for other nonhydrogen atoms, with anomalous dispersion terms applied to the scattering of nickel and phosphorus, resulted in convergence at  $R = 0.057$ ,  $R_w = 0.061$ . Hydrogen atoms were assigned isotropic temperature factors of  $3.0 \text{ \AA}^2$ . Isotropic positional and thermal parameters for the  $[(\text{CO})\text{NiC}_2\text{B}_9\text{H}_{10}\text{PPh}_3]$  unit are listed in Table 2. Anisotropic thermal parameters are given in supplementary material. Atomic labels correspond to those in Figure 5. The most important interatomic distances and angles are listed in Tables III and IV.

The final observed and calculated structure factors are available as supplementary material. The atoms of the polyhedron were labeled according to the nomenclature set forth by IUPAC<sup>22</sup> for boron compounds.



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**Supplemental Material Available:** Listings of observed and calculated structure factor amplitudes, hydrogen positional parameters, and anisotropic thermal parameters (    pages). Ordering information is given on any current masthead page.

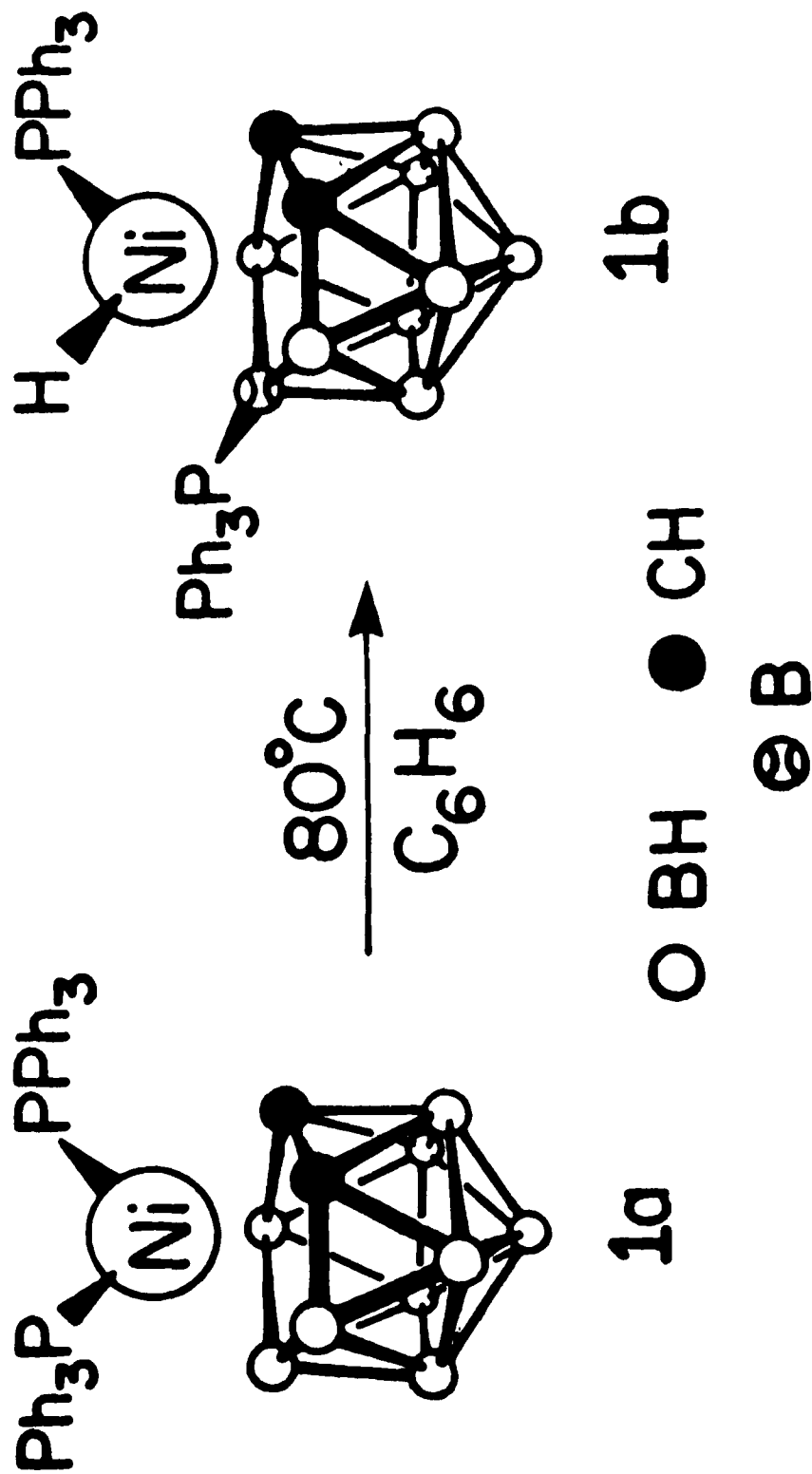
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Figure Captions

1. Ligand Migration Reaction
2. Numbering Scheme for the Nickelacarborane Complexes Prepared. 1a:  $L_1 = L_2 = PPh_3$ ; 2a:  $L_1 = L_2 = P(p\text{-tolyl})_3$ ; 3:  $L_1 = L_2 = PEt_3$ ; 4:  $L_1 = L_2 = PPh_2Me$ ; 5:  $L_1 = L_2 = PPhMe_2$ ; 6:  $L_1, L_2 = PPh_2(CH_2)_3PPh_2$ ; 7:  $L_1 = PPh_3, L_2 = CO$ ; 8:  $L_1 = PPh_3, L_2 = C_5H_5N$ ; 1b:  $L = PPh_3, X = H$ ; 2b:  $L = P(p\text{-tolyl})_3, X = H$ ; 11:  $L = PPh_3, X = Cl$ .
3. Derivative Chemistry of 1b.
4. Derivative Chemistry of 1a.
5. Structure of [closo-3- $\mu$ -CO-8- $PPh_3$ -3,1,2- $NiC_2B_9H_{10}$ ] $_2$ . Thermal ellipsoids are at 50% probability. Hydrogen atoms have been omitted for clarity.
6. Possible Mechanism for the Migration Reaction.





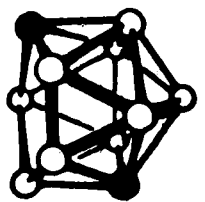
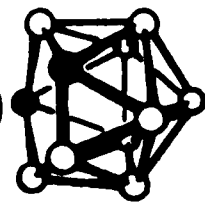
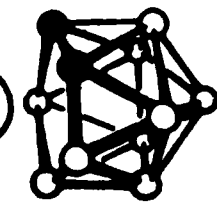
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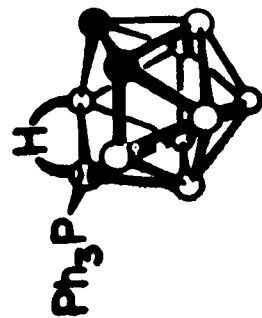
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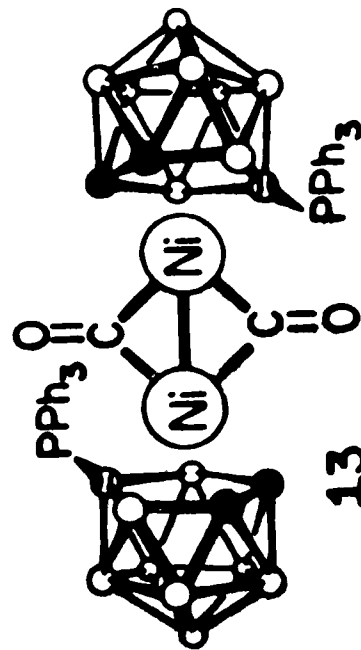
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1b, 2b, 11

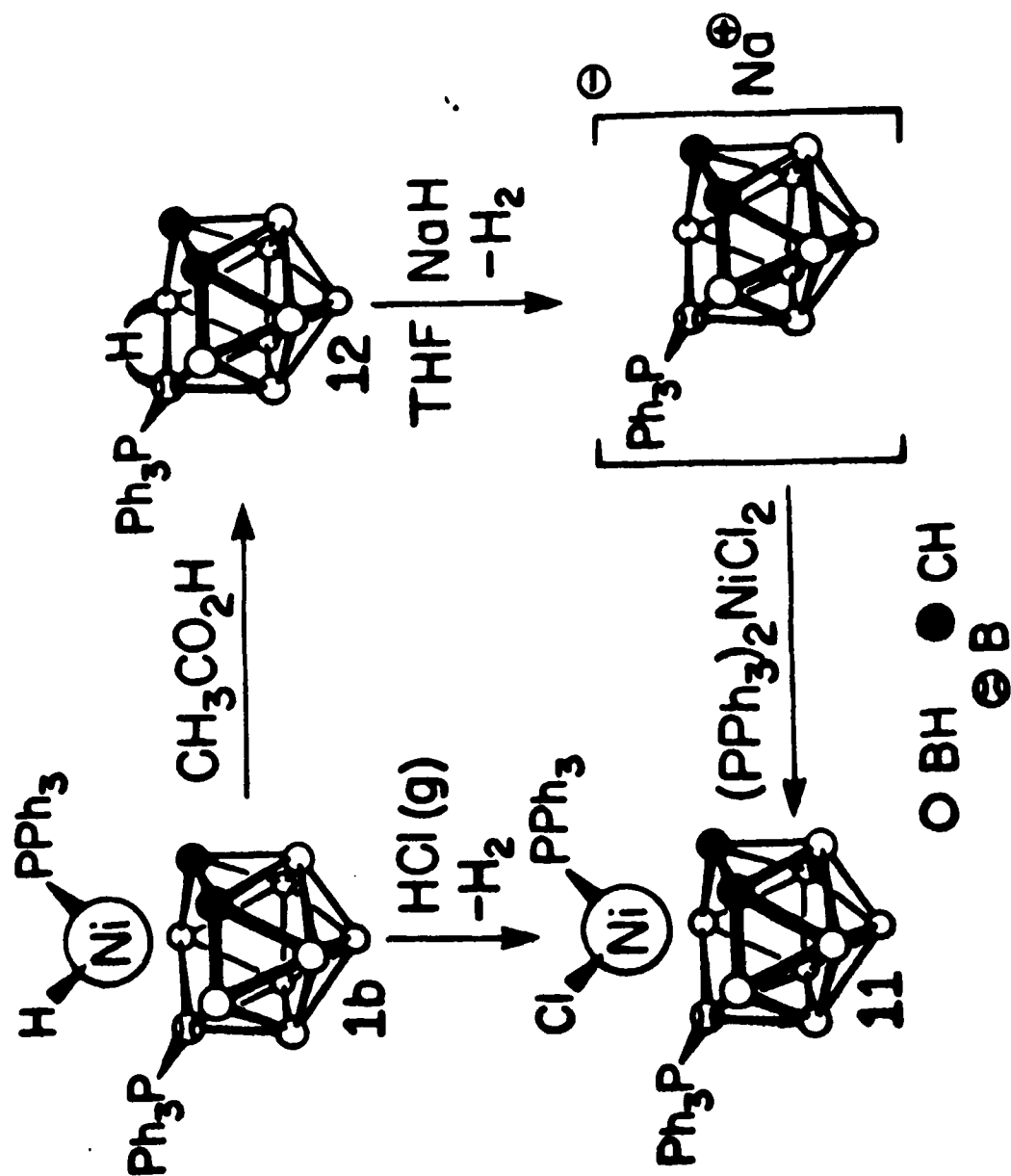


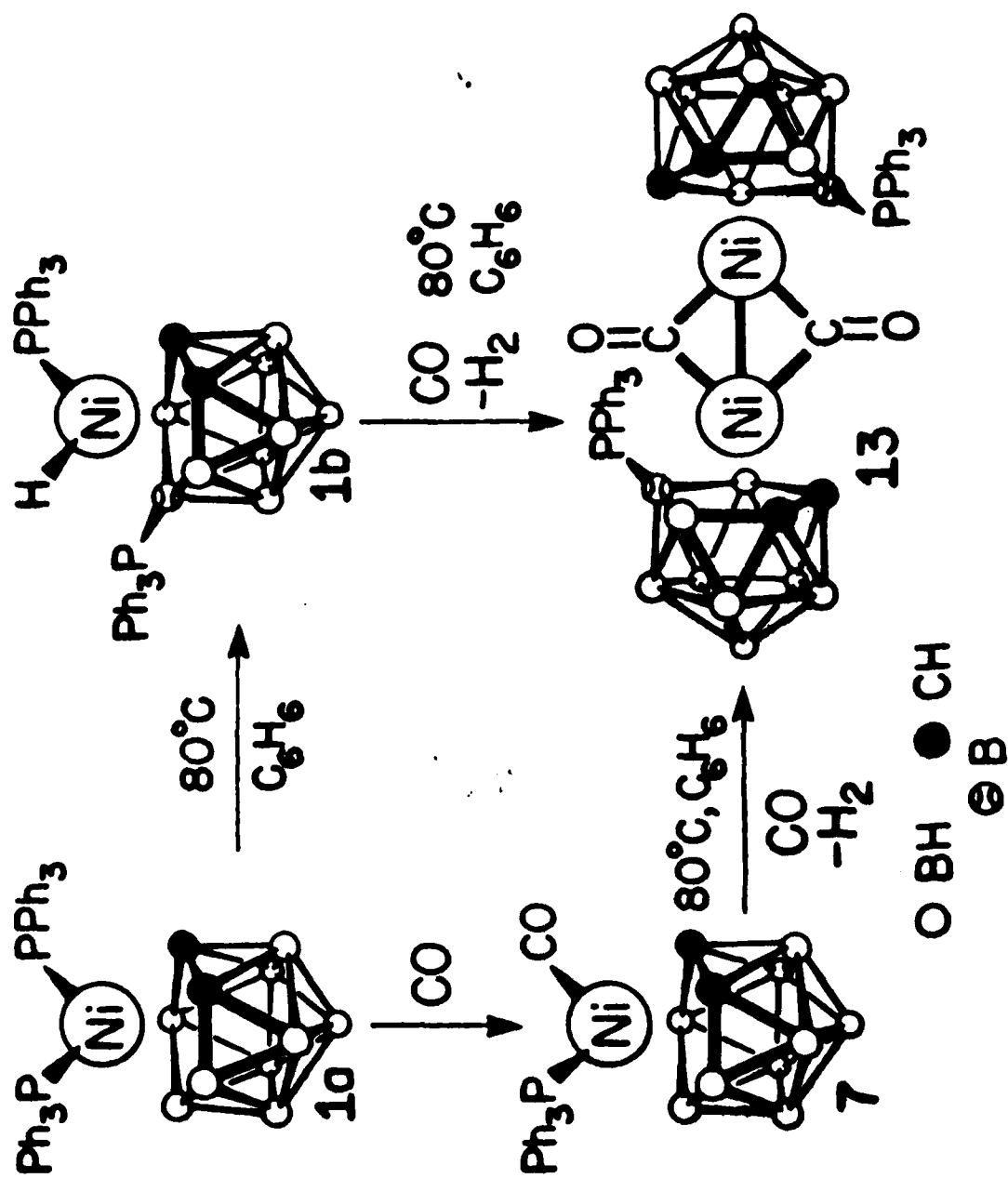
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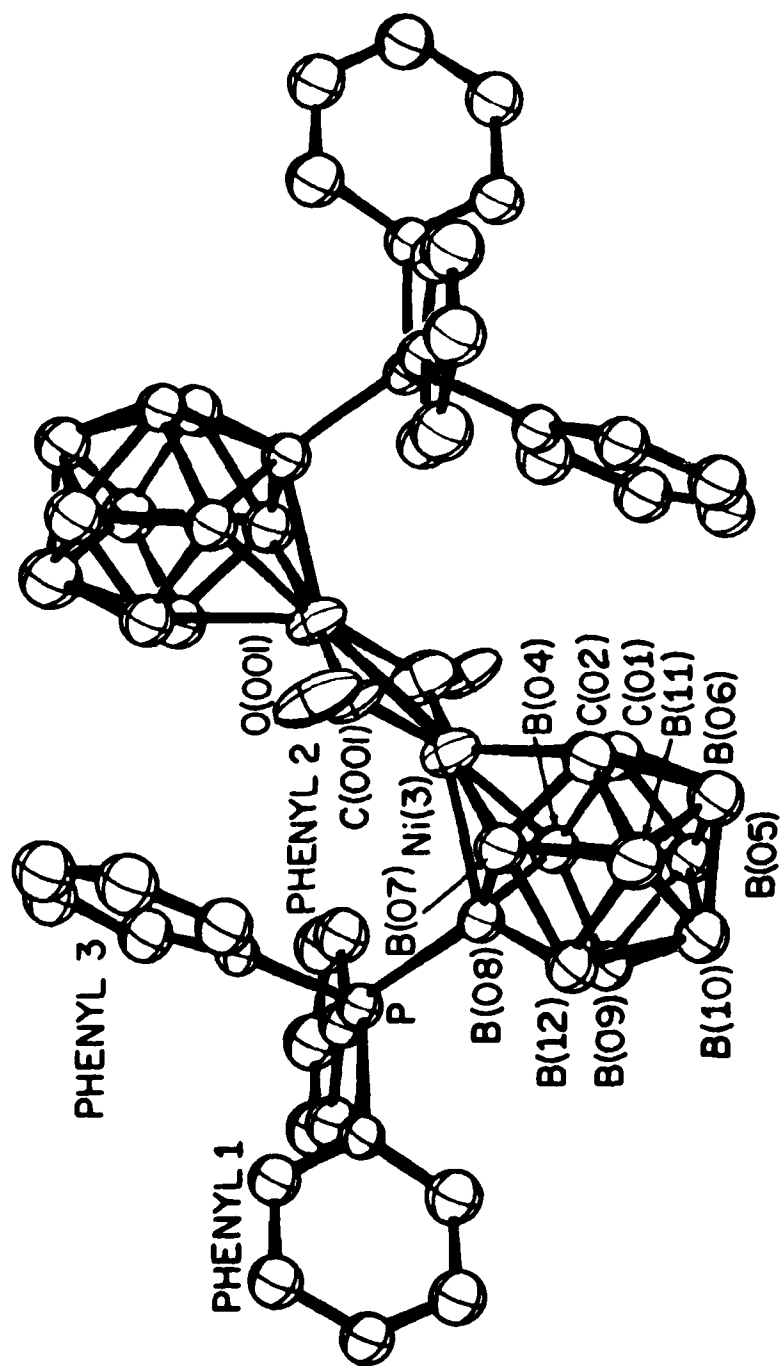
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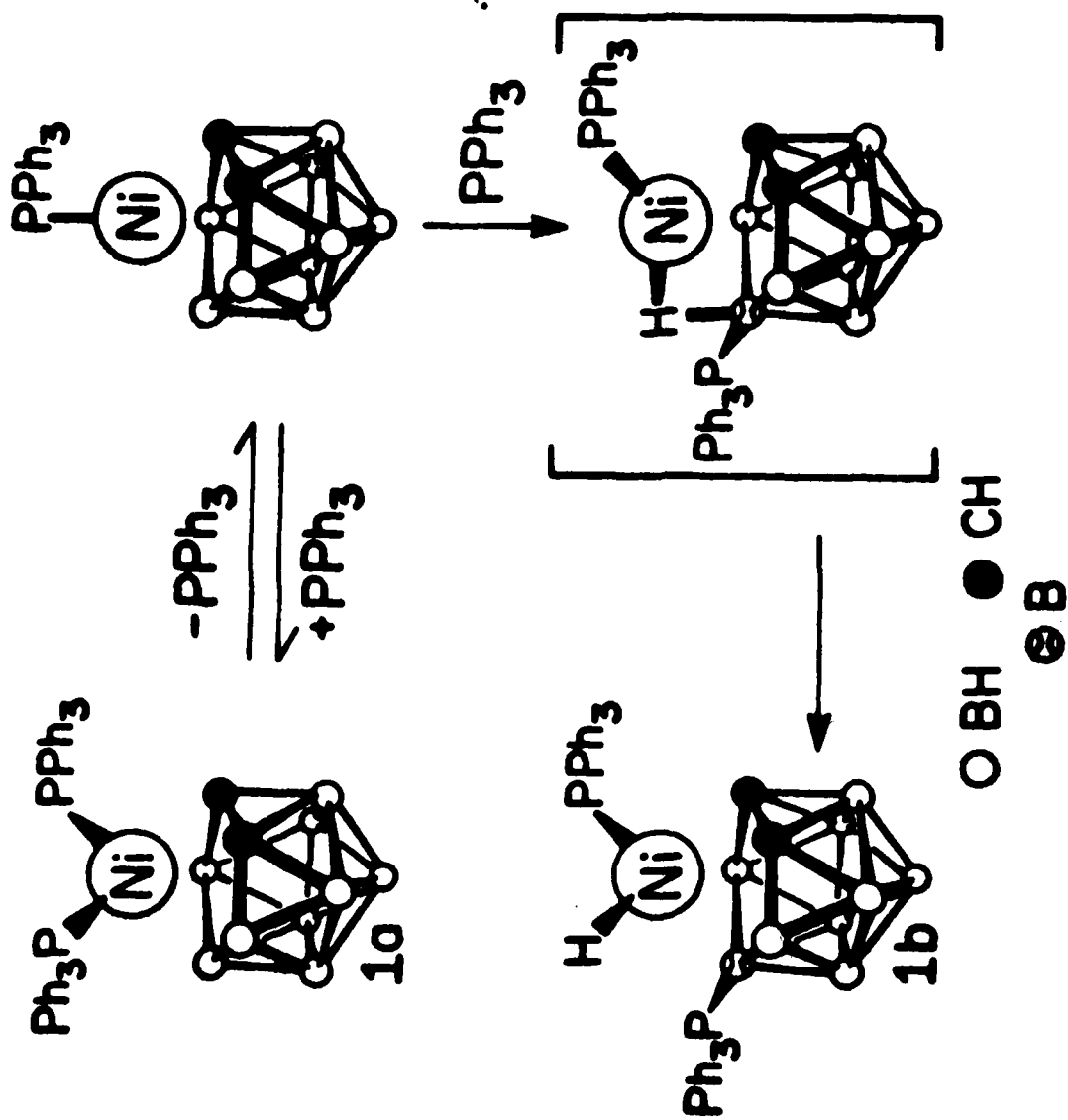


Table I

Crystallographic Data for the Nickelacarborane Dimer  
 $\text{Closo-}(-3-\mu\text{-CO-8-PPh}_3\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{10})_2$

Crystal System: triclinic,  $\bar{1}$ ,  $Z = 1$

Unit Cell:  $a = 13.319(4)$   
 $b = 10.039(3)$   
 $c = 9.813(3) \text{ \AA}$   
 $\alpha = 80.00(1)$   
 $\beta = 82.91(1)$   
 $\gamma = 110.32(1)^\circ$

Observed density (298° K):  $1.265 \text{ g cm}^{-3}$

Data collected @ 298° K

Collection limit (2 $\theta$ ): 50° (MoK $\alpha$ )

Agreement factors:  $R = 0.057$

$R_w = 0.061$

Goodness of fit (GOF): 1.60

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

$$w = 1/\sigma^2(|F_o|)$$

$$\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$$

Table II.

Positional Parameters (fractional coordinates) and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of the Nickel Dimer

| Atom  | X          | Y           | Z          | B        |
|-------|------------|-------------|------------|----------|
| C(01) | 0.0281( 6) | 0.1431( 8)  | 0.1793( 7) | 3.25(15) |
| C(02) | 0.0570( 5) | 0.2724( 7)  | 0.2571( 7) | 2.99(14) |
| B(04) | 0.1213( 7) | 0.0625( 9)  | 0.1811( 9) | 2.81(16) |
| B(05) | 0.1167( 7) | 0.1816(10)  | 0.0281( 9) | 3.59(18) |
| B(06) | 0.0732( 7) | 0.3169(10)  | 0.0752(10) | 3.90(19) |
| B(07) | 0.1767( 6) | 0.2993( 8)  | 0.3182( 8) | 2.47(15) |
| B(08) | 0.2251( 6) | 0.1678( 8)  | 0.2632( 8) | 2.22(14) |
| B(09) | 0.2429( 6) | 0.2028( 8)  | 0.0774( 8) | 2.60(15) |
| B(10) | 0.2134( 7) | 0.3615( 9)  | 0.0135( 9) | 3.02(16) |
| B(11) | 0.1689( 7) | 0.4174( 9)  | 0.1642( 9) | 3.29(17) |
| B(12) | 0.2778( 6) | 0.3515( 8)  | 0.1623( 8) | 2.41(15) |
|       |            |             |            |          |
| C1    | 0.3826( 5) | 0.2079( 7)  | 0.4737( 7) | 2.28(12) |
| C2    | 0.4940( 6) | 0.2710( 8)  | 0.4685( 7) | 3.33(15) |
| C3    | 0.5304( 6) | 0.3486( 8)  | 0.5723( 8) | 4.32(17) |
| C4    | 0.4587( 7) | 0.3619( 9)  | 0.6715( 9) | 4.56(18) |
| C5    | 0.3481( 6) | 0.3023( 8)  | 0.6784( 8) | 4.36(17) |
| C6    | 0.3088( 6) | 0.2219( 7)  | 0.5781( 8) | 3.35(15) |
|       |            |             |            |          |
| C7    | 0.2641( 5) | -0.0889( 7) | 0.4484( 7) | 2.44(13) |
| C8    | 0.2110( 6) | -0.1975( 8) | 0.3822( 8) | 3.67(16) |
| C9    | 0.1655( 6) | -0.3453( 8) | 0.4566( 8) | 4.12(17) |
| C10   | 0.1732( 6) | -0.3824( 8) | 0.5940( 8) | 4.15(17) |
| C11   | 0.2243( 6) | -0.2786( 8) | 0.6616( 8) | 4.03(16) |
| C12   | 0.2702( 6) | -0.1298( 8) | 0.5906( 8) | 3.47(15) |
|       |            |             |            |          |
| C13   | 0.4449( 5) | 0.1085( 7)  | 0.2281( 7) | 2.25(12) |
| C14   | 0.4795( 5) | -0.0063( 7) | 0.2388( 7) | 2.77(14) |
| C15   | 0.5723( 6) | 0.0039( 7)  | 0.1487( 7) | 3.17(14) |
| C16   | 0.6300( 6) | 0.1286( 8)  | 0.0468( 7) | 3.34(15) |
| C17   | 0.5958( 6) | 0.2444( 8)  | 0.0324( 8) | 3.84(16) |
| C18   | 0.5037( 6) | 0.2355( 7)  | 0.1229( 7) | 3.22(15) |
|       |            |             |            |          |
| C001  | 0.0160( 6) | 0.1229( 8)  | 0.5641( 8) | *        |
| O001  | 0.0347( 5) | 0.2247( 6)  | 0.6099( 6) | *        |
| Ni3   | 0.0596( 1) | 0.0797( 1)  | 0.3870( 1) | *        |
| P08   | 0.3273( 1) | 0.1004( 2)  | 0.3497( 2) | *        |

\* Anisotropic thermal parameters are given for these atoms in Supplementary Material.

Table III.

Selected Distances (Angstroms) in  
 $[\text{closo-3-}\mu\text{-CO-8-PPh}_3\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{10}]_2$

| From   | To     | Dist. (e.s.d.) |      | From  | To     | Dist. (e.s.d.) |      |
|--------|--------|----------------|------|-------|--------|----------------|------|
| C(02)  | Ni(3)  | 2.138          | (7)  | B(12) | B(8)   | 1.780          | (10) |
| C(01)  | Ni(3)  | 2.163          | (7)  | B(12) | B(9)   | 1.784          | (11) |
| B(8)   | Ni(3)  | 2.175          | (8)  | B(4)  | C(01)  | 1.701          | (10) |
| B(7)   | Ni(3)  | 2.141          | (8)  | B(4)  | B(5)   | 1.771          | (12) |
| B(4)   | Ni(3)  | 2.144          | (8)  | B(4)  | B(9)   | 1.776          | (11) |
|        |        |                |      | B(4)  | B(8)   | 1.799          | (11) |
| C(001) | O(001) | 1.149          | (8)  | B(5)  | C(01)  | 1.672          | (11) |
| Ni(3)  | Ni(3)  | 2.477          | (2)  | B(5)  | B(9)   | 1.758          | (12) |
| C(001) | Ni(3)  | 1.870          | (8)  | B(5)  | B(6)   | 1.759          | (12) |
| C(001) | Ni(3)  | 1.932          | (8)  | B(6)  | C(01)  | 1.718          | (11) |
|        |        |                |      | B(6)  | C(02)  | 1.730          | (11) |
| C(1)   | P(08)  | 1.821          | (6)  | B(7)  | C(02)  | 1.722          | (10) |
| C(13)  | P(08)  | 1.816          | (6)  | B(7)  | B(8)   | 1.791          | (10) |
| C(7)   | P(08)  | 1.818          | (7)  | B(8)  | B(9)   | 1.765          | (11) |
| B(8)   | P(08)  | 1.938          | (8)  | C(01) | C(02)  | 1.576          | (9)  |
|        |        |                |      | C(01) | H(01)  | 1.023          |      |
| B(10)  | B(6)   | 1.762          | (12) | C(02) | H(02)  | 1.033          |      |
| B(10)  | B(5)   | 1.785          | (12) | B(4)  | H(04)  | 1.140          |      |
| B(10)  | B(12)  | 1.788          | (11) | B(5)  | H(05)  | 1.075          |      |
| B(10)  | B(11)  | 1.777          | (11) | B(6)  | H(06)  | 1.035          |      |
| B(10)  | B(9)   | 1.798          | (11) | B(7)  | H(07)  | 1.116          |      |
| B(11)  | C(02)  | 1.694          | (10) | B(9)  | H(09)  | 1.037          |      |
| B(11)  | B(6)   | 1.759          | (12) | B(10) | H(010) | 1.187          |      |
| B(11)  | B(12)  | 1.791          | (11) | B(11) | H(011) | 1.075          |      |
| B(11)  | B(7)   | 1.790          | (11) | B(12) | H(012) | 1.089          |      |
| B(12)  | B(7)   | 1.775          | (11) |       |        |                |      |

Table IV

Selected Angles (degrees) in  
 $[\text{closo-3-}\mu\text{-CO-8-PPh}_3\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{10}]_2$

|        |        |       |            |        |       |        |            |
|--------|--------|-------|------------|--------|-------|--------|------------|
| C(01)  | B(4)   | B(8)  | 105.61(53) | C(001) | N1(3) | C(001) | 98.72(31)  |
| C(01)  | B(4)   | N1(3) | 67.34(36)  | C(001) | N1(3) | N1(3)  | 50.43(25)  |
| B(8)   | B(4)   | N1(3) | 66.26(35)  | C(001) | N1(3) | C(02)  | 95.40(30)  |
| C(02)  | B(7)   | B(8)  | 104.98(52) | C(001) | N1(3) | B(7)   | 88.82(30)  |
| C(02)  | B(7)   | N1(3) | 66.17(34)  | C(001) | N1(3) | B(4)   | 172.30(32) |
| B(8)   | B(7)   | N1(3) | 66.47(35)  | C(001) | N1(3) | C(01)  | 130.87(30) |
| B(9)   | B(8)   | P(08) | 117.70(46) | C(001) | N1(3) | B(8)   | 125.27(30) |
| B(12)  | B(8)   | P(08) | 116.63(46) | C(001) | N1(3) | N1(3)  | 48.28(24)  |
| B(7)   | B(8)   | B(4)  | 105.34(52) | C(02)  | N1(3) | B(7)   | 47.45(27)  |
| B(7)   | B(8)   | P(08) | 123.91(48) | C(02)  | N1(3) | B(4)   | 78.70(28)  |
| B(7)   | B(8)   | N1(3) | 64.51(34)  | C(02)  | N1(3) | C(01)  | 42.99(24)  |
| B(4)   | B(8)   | P(08) | 125.36(47) | C(02)  | N1(3) | B(8)   | 80.49(26)  |
| B(4)   | B(8)   | N1(3) | 64.50(35)  | C(02)  | N1(3) | N1(3)  | 131.09(19) |
| P(08)  | B(8)   | N1(3) | 114.83(36) | B(7)   | N1(3) | B(4)   | 83.54(30)  |
|        |        |       |            | B(7)   | N1(3) | C(01)  | 78.91(28)  |
| O(001) | C(001) | N1(3) | 142.04(66) | B(7)   | N1(3) | B(8)   | 49.02(28)  |
| O(001) | C(001) | N1(3) | 136.60(63) | B(7)   | N1(3) | N1(3)  | 136.12(22) |
| N1(3)  | C(001) | N1(3) | 81.28(31)  | B(4)   | N1(3) | C(01)  | 46.51(28)  |
|        |        |       |            | B(4)   | N1(3) | B(8)   | 49.24(29)  |
| C(02)  | C(01)  | B(4)  | 111.83(55) | B(4)   | N1(3) | N1(3)  | 139.41(25) |
| C(02)  | C(01)  | N1(3) | 67.63(36)  | C(01)  | N1(3) | B(8)   | 80.01(27)  |
| B(4)   | C(01)  | N1(3) | 66.15(36)  | C(01)  | N1(3) | N1(3)  | 133.05(21) |
| C(01)  | C(02)  | B(7)  | 112.03(53) | B(8)   | N1(3) | N1(3)  | 144.38(22) |
| C(01)  | C(02)  | N1(3) | 69.38(36)  | B(7)   | C(02) | N1(3)  | 66.38(34)  |
| C(1)   | P(08)  | C(7)  | 106.68(29) |        |       |        |            |
| C(1)   | P(08)  | C(13) | 105.75(29) | C(001) | N1(3) | B(8)   | 118.69(30) |
| C(1)   | P(08)  | B(8)  | 111.02(30) | C(001) | N1(3) | C(01)  | 103.20(32) |
| C(7)   | P(08)  | C(13) | 104.96(29) | C(001) | N1(3) | B(4)   | 88.97(31)  |
| C(7)   | P(08)  | B(8)  | 112.40(31) | C(001) | N1(3) | B(7)   | 167.36(30) |
| C(13)  | P(08)  | B(8)  | 115.39(31) | C(001) | N1(3) | C(02)  | 140.63(31) |

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### Abstract

The reaction of  $L_2NiCl_2$  ( $L = PR_3$ ) species with *nido*-7,8-, -7,9-, or -2,9- $C_2B_9H_{11}^{2-}$  ions led to the formation of the corresponding icosahedral bis(phosphine)nickelacarboranes in high yield. Heating members of the *closa*-3,3-(triarylphosphine) $_2$ -3,1,2- $NiC_2B_9H_{11}$  series at 80° C in benzene solution led to the formation of the corresponding [*closa*-3,8-(triarylphosphine) $_2$ -3-H-3,1,2- $NiC_2B_9H_{11}$ ] by interchange of phosphine and hydrido ligands. No intermediates were observed and the reaction was specific for the bis(triarylphosphine)-3,1,2- $NiC_2$  icosahedral system among those investigated. A dimeric nickelacarborane carbonyl [*closa*-(3- $\mu$ -CO-8- $PPh_3$ -3,1,2- $NiC_2B_9H_{11}$ ) $_2$ ] was prepared by a variety of routes such as the reaction of [*closa*-3,3-( $PPh_3$ ) $_2$ -3,1,2- $NiC_2B_9H_{11}$ ] (1a), with CO in benzene at 80° C. A variety of ligand substitution reactions were carried out with 1a. The mechanism of the phosphine-hydride ligand interchange is discussed. The dimeric nickelacarborane complex was characterized by an X-ray diffraction study. Amber crystals were triclinic, space group  $P\bar{1}$ , with  $a = 13.319(4)$ ,  $b = 10.039(3)$ ,  $c = 9.813(3)$  Å,  $\alpha = 80.00(1)^\circ$ ,  $\beta = 82.91(1)^\circ$ ,  $\gamma = 110.32(1)^\circ$ , and  $Z = 1$ . The structure was solved by conventional heavy atom methods to a final discrepancy index of  $R = 0.057$  for 2233 independent observed reflections. The complex contains a metal-metal bond (2.477(2) Å) and two metal-bridging carbon monoxide groups.



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